# X-ray-scattering study of copper magnetism in nonsuperconducting $PrBa_2Cu_3O_{6.92}$

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X-ray magnetic scattering from ordered Cu spins has been observed in a high-$T_c$ compound. The measurements were made on the anomalous cuprate $PrBa_2Cu_3O_{6.92}$ with x-ray photon energies tuned in the vicinity of the Cu $K$ edge. The high wave-vector resolution enabled us to observe an incommensurate double-$Q$ Cu spin structure below $T_{Pr}=19$ K that forms as a result of coupling between the magnetically ordered Cu and Pr sublattices. Above $T_{Pr}$, the Cu ordering is commensurate, ruling out static spin-charge stripe order as an explanation for the absence of superconductivity in this material.

Magnetism in Cu-containing compounds has been intensively studied following the discovery of high-$T_c$ superconductivity in the layered cuprates. Many interesting and novel phenomena involving Cu magnetism have subsequently been observed in other low dimensional architectures. Examples are quasi-one-dimensional spin chains, e.g., $KCuF_3$ (Ref. 1) and $Sr_2CuO_3$,[2] spin Peierls systems, e.g., $CuGeO_3$,[3] and spin-ladder compounds, e.g., $Sr_{n-1}Cu_{n+1}O_{2n}$.[4] The existence of unusual ground states in these systems is due to the low-spin state ($S=\frac{1}{2}$) of the $Cu^{2+}$ ion which leads to strong quantum fluctuations.

Until now, neutron scattering has been the only technique available for studying the Cu spin structures in these materials. While this technique has important strengths, including the ability to study both static and dynamic fluctuations quantitatively, it also has limitations. For example, the neutron scatters from all magnetic moments in the system, which can lead to ambiguities when there are two or more magnetic species present, and large volume samples are often required.

X-ray magnetic scattering is in many respects complementary to neutron scattering, and is becoming an increasingly important probe of magnetism. Particular strengths of the technique include, (i) element specificity, allowing multiple magnetic sublattices to be studied in a model-independent manner, (ii) high reciprocal space resolution, and (iii) the ability to study very small volume samples. The last of these is particularly useful in the study of new materials, for which high-quality samples are often small. In addition, the relatively poor energy resolution means that inelastic fluctuations are integrated, ensuring that the quasielastic approximation is valid even in materials such as the high-$T_c$ superconductors which have large energy scales.[5]

The ability to use x-ray magnetic scattering to examine novel cuprates would therefore be very valuable. To date, however, there have been no x-ray studies of Cu magnetism. This is in part because the $L$ and $M$ edges, which give large resonant enhancements in the x-ray magnetic scattering cross section and which have been utilized to such advantage in the study of magnetism in rare earths and actinides,[6–8] fall below $\sim 1$ keV for transition metal compounds. Moreover, the nonresonant scattering, i.e., that far from an absorption edge, is weak.

 

By utilizing a small resonant enhancement at the $K$ edge[9,10] we have now succeeded in observing Cu-site magnetic order, in the anomalous cuprate $PrBa_2Cu_3O_{6+x}$. Magnetic peaks on the order of 10 counts $s^{-1}$ were observed. The results provide new insights into the magnetism of $PrBa_2Cu_3O_{6+x}$, and open up a new and potentially important window on cuprate magnetism.

$PrBa_2Cu_3O_{6+x}$ has attracted attention as the nonsuperconducting member of the $(R)Ba_2Cu_3O_{6+x}$ series, where $R = Y$ or trivalent rare earth.[11] Recent interest has centered on the magnetism about which are a number of outstanding questions that can only be addressed by a high resolution, element specific probe. These arise from the fact that it contains two magnetic sublattices, and from recent x-ray scattering work which revealed the presence of an incommensurate modulation on the Pr sublattice.[12] This unusual ordering is important because of the insight it provides into the nature of this anomalous compound in relation to other members of the series. Specifically, $PrBa_2Cu_3O_{6+x}$ is antiferromagnetic and nonsuperconducting for all $x$, with the copper spins ordering at $T_N(x) = 250–350$ K.[13–15] Further, the Pr moments order at very high temperatures ($T_{Pr} = 10–19$ K, depending on $x$) relative to the other members, for which $T_R = 0–2$ K. These features, together with theoretical models for the suppression of superconductivity based on hybridization schemes,[16,17] have provoked a great deal of work on the magnetic ground states of this system.

The recently discovered incommensurate magnetism on the Pr sublattice raises new questions. The modulation is static, with a wave vector $(0.5\pm\delta,0.5,0)$ or $(0.5,0.5\pm\delta,0)$, $\delta = 0.006–0.008$ r.l.u.,[12,18] and is thus reminiscent of those seen in ''214'' superconductors, such as $La_{1.6-x}Nd_{0.4}Sr_xCuO_4$. In the 214 materials, these modulations have been associated with the suppression of superconductivity through the presence of stripe correlations,[19–21] which raises the interesting possibility that, despite fundamental differences between the two systems, the same mechanism may be active in $PrBa_2Cu_3O_{6+x}$[12]. A crucial question in such a scenario is whether the Cu site magnetism is also incommensurate. This question can only be answered definitively by the x-ray-scattering technique.

The high-resolution measurements reported here demonstrate that the Cu spins in fact form a commensurate antiferromagnetic structure between $T_N = 275$ K and $T_{Pr} = 19$ K, but that below $T_{Pr}$ a complex 2-$Q$ magnetic structure appears on the Cu sublattice, with the same incommensurate modulation as the Pr sublattice. These results confirm that a strong coupling between the Pr and Cu sublattices exists,[15] and imply that the suppression of superconductivity in $PrBa_2Cu_3O_{6+x}$ does not arise from the stripe correlation mechanism.

The present work was begun on the wiggler source, X25 at the National Synchrotron Light Source, with the bulk of the data being taken on the undulator source, ID20 at the European Synchrotron Radiation Facility. This latter beamline is comprised of a double bounce Si(111) monochromator and two mirrors to provide focusing and harmonic rejection. A flux of $4\times10^{12}$ photons $s^{-1}$ was delivered in a $0.3\times0.3$ mm spot with an energy resolution of 1.2 eV at 9 keV.[22] The samples used were the same as those of Ref. 12, with oxygen content $x = 0.92$. They consist of small (2–4 $mm^2$ by 0.1 mm) platelets with a $c$-axis surface normal, and mosaic spreads of $\approx 0.05°$ [full width at half maximum (FWHM)]. They were mounted such that peaks of the form $(h,h,l)$ were in the diffraction plane, though scans could be performed in arbitrary directions through such peaks.

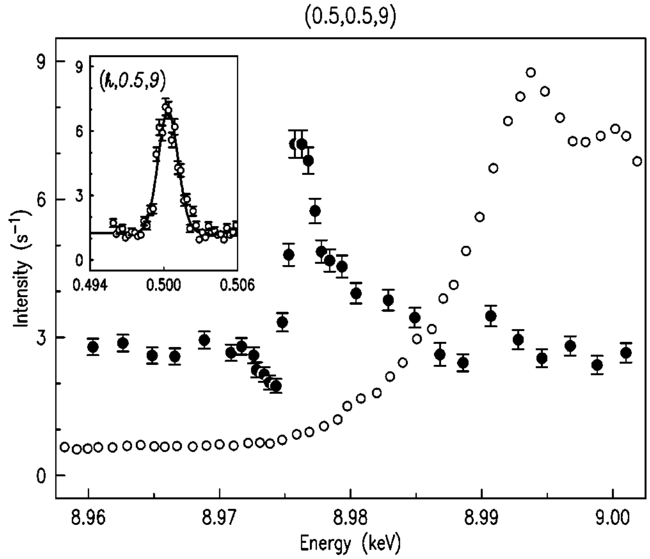


FIG. 1. Intensity of the (0.5,0.5,9) antiferromagnetic Bragg peak as a function of incident photon energy (closed circles). Open circles: Cu fluorescence. Inset: $h$ scan through the (0.5,0.5,9) antiferromagnetic Bragg point measured at the peak of the resonance. All data were taken at $T = 20$ K.

In order to observe the x-ray magnetic scattering from the Cu spin system, we followed the approach taken in recent work on NiO (Ref. 10) and searched for a resonant enhancement in the scattering in the vicinity of the Cu $K$ edge. At $T = 20$ K (i.e., above $T_{Pr}$) a scan through the (0.5,0.5,9) antiferromagnetic zone center revealed a single resolution-limited peak of about 6 counts $s^{-1}$ (inset to Fig. 1). The intensity of this reflection as the incident energy was tuned through the Cu $K$ edge is shown in Fig. 1. A small resonant enhancement of a factor of $\approx 2–3$ is observed at 8976 eV, about 17 eV below the peak in the fluorescence. This enhancement, and the position of the resonance relative to the peak of the fluorescence, are both similar to that observed in NiO and are consistent with magnetic scattering arising from a quadrupolar ($1s \leftrightarrow 3d$) resonance. Note that the scattered intensity away from the resonance is nonzero, and thus we believe we have also observed nonresonant magnetic scattering from the Cu.[23] The asymmetry in the resonance line shape, apparent in Fig. 1, is then attributed to the interference between the nonresonant and resonant scattering. Thus the data of Fig. 1 are strongly suggestive of the observation of x-ray magnetic scattering from a commensurate Cu sublattice.

There are, however, a number of other potential scattering mechanisms, which must be ruled out as the origin of the (0.5,0.5,9) scattering. One important test is to determine the intensity variation with $l$, the component of the scattering vector along the $c$ axis. Scattering from the Cu spins on the $CuO_2$ layers should show a sinusoidal variation with $l$, arising from the presence of two $CuO_2$ layers (i.e., a bilayer) in

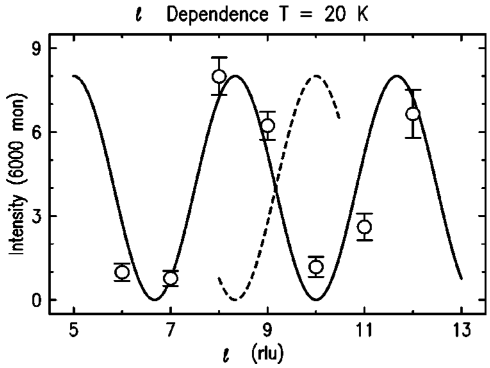


FIG. 2. Intensity of $(0.5,0.5,l)$ peaks for a number of $l$ values. The solid line is the antiferromagnetically coupled bilayer magnetic structure factor $\sin^2(\pi z l)$, with $z=0.3$. The dashed line is the ferromagnetically coupled structure factor, $\cos^2(\pi z l)$.

each unit cell. For an antiferromagnetically coupled bilayer the intensity should vary as $\sin^2(\pi z l)$ where $z$ is the fractional interplanar separation.

To test this dependence we measured the intensity of the $(0.5,0.5,l)$ Bragg peaks for a number of $l$ values with the incident energy set to 8976 eV. The results of these measurements are shown in Fig. 2, along with the function $\sin^2(\pi z l)$, with $z=0.3$.[11] Clearly, the observed scattering has the requisite behavior.

In addition, while in general complex,[24] the polarization dependence of x-ray magnetic scattering at a quadrupole resonance contains contributions which should rotate the linearly polarized component of the photon by 90°. We have performed polarization analysis of the observed scattering, utilizing a LiF crystal as a polarization analyzer ($\theta_{\mathrm{Bragg}}=43.3°$). While the mosaic of this crystal was compromised, preventing quantitative polarization analysis, the results were consistent with a significant rotated component to the scattering. We conclude that the observed scattering at $(0.5,0.5,l)$ is magnetic scattering from the Cu sublattice.

We now discuss the behavior of the Cu site magnetism at temperatures above and below $T_{\mathrm{Pr}}$. The peak shown in the inset to Fig. 1 is commensurate and resolution limited, which puts a lower bound on the correlation length of $\xi = 1/\mathrm{HWHM} > 750$ Å.[25] The temperature dependence of this peak, as measured on resonance, is shown in Fig. 3. This intensity is proportional to the square of the order parameter and shows a Néel temperature of $\approx 275$ K, consistent with previous measurements.[15] For all temperatures above 20 K the scattering remains commensurate and resolution limited.

On further cooling, however, we find an abrupt change in the copper scattering at $T_{\mathrm{Pr}}$. The intensity of the (0.5,0.5,9) reflection drops to approximately half its previous value, with no change in the position or width, signaling that intensity has been lost from the commensurate component. The loss in intensity indicates an in-plane rotation of the Cu spins due to coupling to the Pr magnetic ordering, as discussed previously by Boothroyd *et al.*[15] As the Pr ordering is now known to be incommensurate for $9\,\mathrm{K} < T < T_{\mathrm{Pr}}$,[12] it follows that the component of the Cu spins coupled to the Pr should also be incommensurate, and from the proposed pseudodipolar symmetry of the Pr-Cu coupling[27] the incommensurate component of the Cu spins should be stacked ferromagnetically along the $c$ axis. The scattering from this component

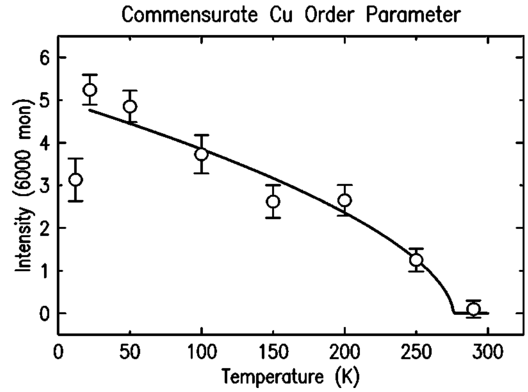


FIG. 3. Temperature dependence of the commensurate Cu scattering at (0.5,0.5,9). The line is a fit to a power law in order to estimate the ordering temperature. The reduction in intensity below 20 K is caused by the reorientation of the bilayer Cu spin structure induced by the magnetic ordering of the Pr sublattice.

should then follow the structure factor for a ferromagnetically coupled bilayer, $\cos^2(\pi z l)$, which peaks at $l=10$ (dashed line, Fig. 2). We, therefore, performed scans in the vicinity of the (0.5,0.5,10) antiferromagnetic Bragg point. An $h$ scan through (0.5,0.5,10) is shown in Fig. 4, together with the same scan at $l=9$. A single commensurate peak is observed at $l=9$, whereas at $l=10$ additional incommensurate peaks are observed at $(0.5\pm\delta,0.5,10)$ with $\delta\approx 0.007$ r.l.u. These measurements were made at the peak of the Cu $K$-edge resonance, and therefore reflect almost entirely the Cu magnetism.[26]

These results enable us to propose a model for the coupled Pr-Cu magnetic structure. Defining the $x$ axis to be the direction of the Cu spins above $T_{\mathrm{Pr}}$, we find that the simplest structure consistent with the observed scattering is one in which the Pr moments rotate in the $x$-$z$ plane with wave vector $0.5+\delta$ along either $x$ (in which case they form a cycloid) or $y$ (a spiral). The Cu spins then oscillate harmonically in the $x$-$y$ plane about the $x$ axis with the same wave vector as the spiral. The Cu spins reach their maximum angle

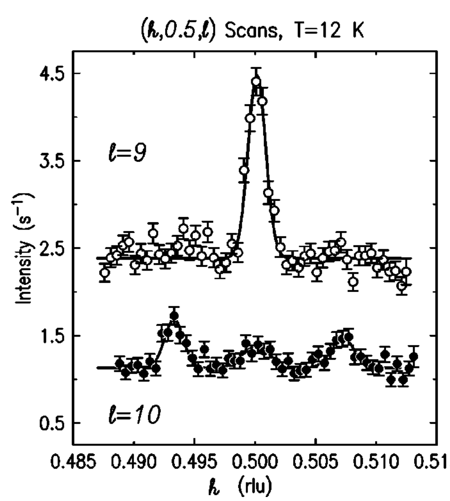


FIG. 4. $h$ scans through $(0.5,0.5,l)$ points at $T=12$ K: $l=9$ (open circles), $l=10$ (closed circles). The $l=9$ data are offset vertically for clarity.

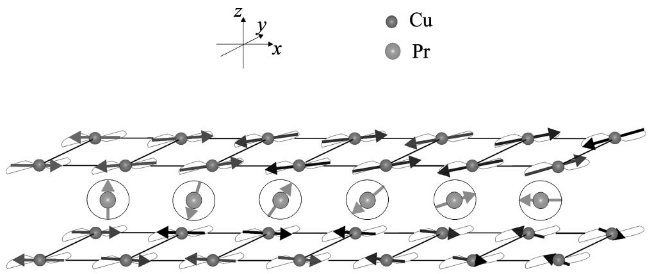


FIG. 5. Schematic drawing of the low-temperature incommensurate magnetic structure of $PrBa_2Cu_3O_{6+x}$ (9 K$<T<T_{Pr}=18$ K). Only the bilayer Cu and Pr atoms are shown for simplicity. The central Pr spins rotate in the *x*-*z* plane with a long period modulation. For illustrative purposes a modulation with a wavelength of 24 chemical unit cells is shown. In the real structure, the modulation wavelength is $\approx 150$ unit cells. The Pr spin structure is described by an ordering wave vector $(0.5\pm\delta,0.5,0)$. The Cu spins form a modulated antiferromagnetic structure which can be regarded as a fan structure propagating along the *x* direction with adjacent Cu spins in the sequence almost, but not quite, antiparallel to one another. Neighboring Cu spins in the *y* direction are exactly antiparallel. In the *z* direction, the *x* components of neighboring spins are antiparallel but the *y* components are parallel. This arrangement of Cu spins is described by two different ordering wave vectors, one (0.5, 0.5, 0) associated with the underlying antiferromagnetic structure, and the other $(0.5\pm\delta,0.5,0)$ arising from the propagation of a twisting distortion in this antiferromagnetic structure along the *x* direction.

to the *x* axis, $\phi_0$, when the Pr moments point along *x*. Although we did not observe higher-order odd harmonics we cannot rule out the possibility of ‘‘bunching’’ of the modulation since the intensities are weak. This model is a refinement of that proposed in Ref. 15, and gives the same level of agreement with the neutron intensities. In the new model we find, $\mu_{Cu}=0.55\pm0.03\mu_B$, $\mu_{Pr}=0.6\pm0.05\mu_B$, and $\phi_0=41\pm5°$.

A schematic drawing of this structure is shown in Fig. 5, for the case in which the Pr moments form a cycloid propagating along the *x* direction. Note, as discussed above, the commensurate component of the copper spins (the *x* component) is coupled antiferromagnetically between the two layers of the bilayer, and the incommensurate component (the *y* component) is ferromagnetically coupled within the bilayer.

The significance of the work reported here lies in the fact that it demonstrates that the incommensurability is not a fundamental property of the Cu spin system (since it only appears below $T_{Pr}$). This rules out the possibility that static spin-charge stripe ordering of the type described in Ref. 19 is connected with the absence of superconductivity in $PrBa_2Cu_3O_{6+x}$. While the true origin of the incommensurability remains unclear, a more likely explanation is frustration within the Pr-Pr and Pr-Cu couplings, the latter of which transmits the effect to the Cu sublattice ordering. A second possibility is that the incommensurate order in nonsuperconducting $PrBa_2Cu_3O_{6+x}$ is a property of the chains, since the observed incommensurate ordering vector $(0.5\pm\delta,0.5,0)$ permits coupling of the Pr/Cu spin structure in the $CuO_2$ layers to the Cu spins in the chains. In this context, it is interesting that incommensurate dynamic fluctuations have been observed on the chain sites in $YBa_2Cu_3O_{6+x}$.[28,29] However, we note that no magnetic ordering of the Cu spins in the chains has been observed in our measurements to date, though we cannot rule out a small Cu ordered moment below the level of the current experimental sensitivity.

Finally, these studies illustrate the utility of x-ray magnetic scattering in the study of Cu magnetism. The excellent reciprocal-space resolution enabled us to measure the incommensurate splitting which, because of the length of the period, would not have been resolved by neutron diffraction, and the ability to study the magnetic scattering from Cu independently of that from Pr via resonance effects was crucial in understanding the coupling between the two magnetic sublattices. Thus these measurements point towards the use of x-ray magnetic scattering as a powerful, complementary technique to neutron scattering for the study of Cu magnetism in many other interesting systems.

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[26] The extent of any contribution from nonresonant Pr scattering, which would also produce incommensurate peaks, can be estimated from the $l=9$ scan, since there is no $l$ dependence in the structure factor of the Pr scattering. No significant incommensurate scattering is observed at $l=9$.

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